

A FACILE PREPARATION OF AROMATIC CARBOXYLIC ACID ESTERS
BY THE REACTION OF 1,3-BUTADIENYLAMINE AND 1,3-BUTADIENYL ETHER
WITH ACETYLENE CARBOXYLIC ACID ESTERS

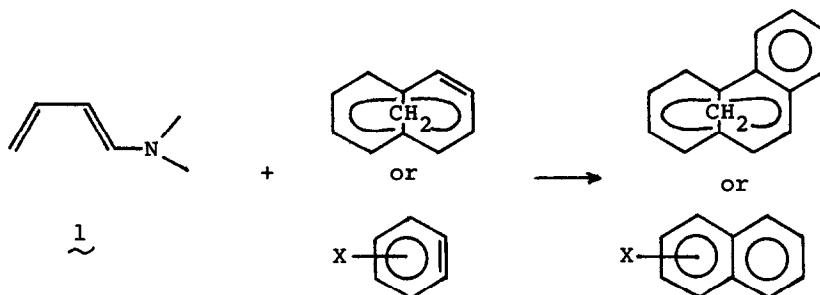
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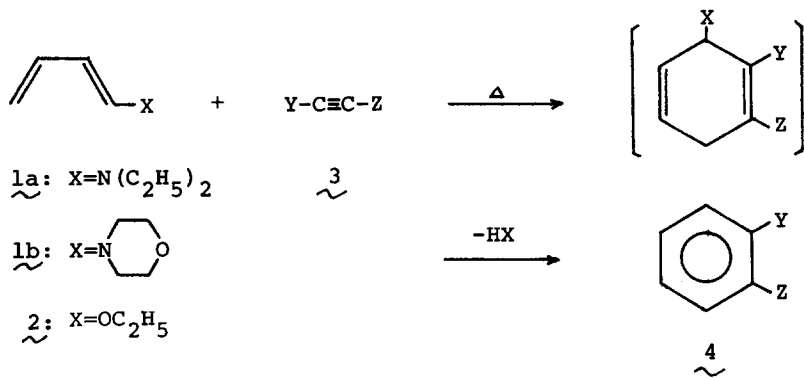
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Very recently, Vogel¹ and Tanimoto² have demonstrated that 1,3-butadienyl-amine (1) reacted with various arynes to condense a new benzene moiety on the arenes in an one-step manner. Now, we describe a facile preparation of aromatic carboxylic acid esters from the cycloaddition of 1 and the alkoxy analog (2) with acetylene carboxylic acid esters.



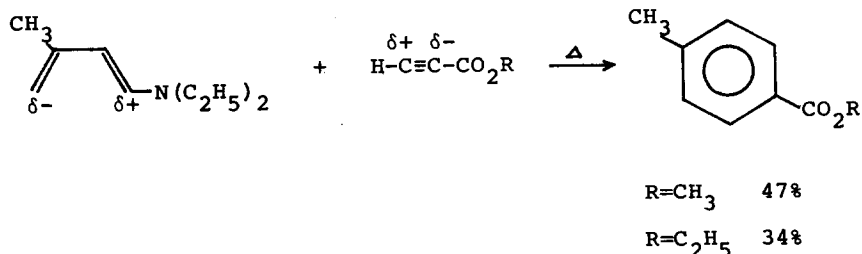
The substituted 1,3-butadienes such as N,N-diethyl-1,3-butadienylamine (1a), 4-(1,3-butadienyl)morpholine (1b) and 1,3-butadienyl ethyl ether 2 reacted readily with acetylene carboxylic acid esters (3) to afford aromatic carboxylic acid esters (4) in a fairly good yield (Table). In all cases the initial cycloadduct intermediate was not detected, because the following deamination or dealcoholation occurred readily. The resulting diethylamine or

morpholine was trapped as an enamine adduct with 3, but for 2 such adduct was not detected.

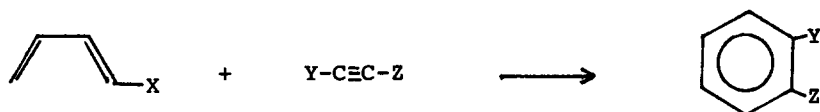


The reaction of acetylene dicarboxylic acid esters with these substituted butadienes gave the adducts in higher yields than the reaction of acetylene monocarboxylic acid esters except for the case of 2 at a much higher temperature. On the other hand, phenylacetylene and ethyl phenylpropiolate gave no adduct with the butadienes. These facts seem to indicate a higher reactivity of an electron-poor acetylene toward the substituted butadienes. However, highly reactive dicyanoacetylene gave phthalonitrile in only 9% yield even in the controlled condition at -78°C accompanied with a formation of a large amount of polymeric substance.

N, N-Diethyl-3-methyl-1,3-butadienylamine was prepared in order to determine the direction of cycloaddition of these substituted butadienes.³ The 3-methyl substituted butadienylamine was refluxed with acetylene monocarboxylic acid ester in ether for 12 hrs. p-Toluic acid ester was found to be a sole product by GLC, and a trace of ortho-isomer could not be detected. This



Table



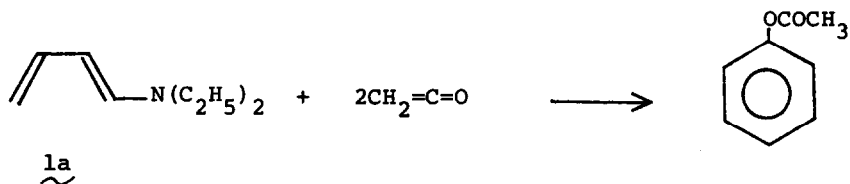
X	Y, Z	Reaction time (hrs)	Temperature (°C)	Yield ^a (%)
$N(C_2H_5)_2$	$Y=Z=CO_2CH_3^b$	5	36 ^d	58 ^f
	$Y=Z=CO_2C_2H_5^b$	5	36 ^d	70 ^g
	$Y=H, Z=CO_2CH_3^b$	5	36 ^d	31 ^f
	$Y=H, Z=CO_2C_2H_5^b$	5	36 ^d	23 ^f
	$Y=Z=CN^b$	5	36 ^d	4 ^g
	$Y=Z=CN^b$	5	-78 ^d	9 ^f
	$Y=Z=CO_2CH_3^b$	5	36 ^d	77 ^g
	$Y=Z=CO_2C_2H_5^b$	5	36 ^d	63 ^f
	$Y=H, Z=CO_2CH_3^b$	10	36 ^d	2 ^f
	$Y=H, Z=CO_2C_2H_5^b$	10	36 ^d	trace ^f
OC_2H_5	$Y=Z=CO_2CH_3^c$	10	140 ^e	44 ^f
	$Y=Z=CO_2C_2H_5^c$	10	140 ^e	37 ^f
	$Y=H, Z=CO_2CH_3^c$	10	140 ^e	44 ^g
	$Y=H, Z=CO_2C_2H_5^c$	10	140 ^e	60 ^g
	$Y=Z=CN^c$	5	-78 ^e	4 ^g

^aAll products were identified on ¹H NMR and GLC. ^bA 1:2 molar ratio of butadiene/acetylene. ^cAn equivalent molar ratio of butadiene/acetylene. ^dIn ether.

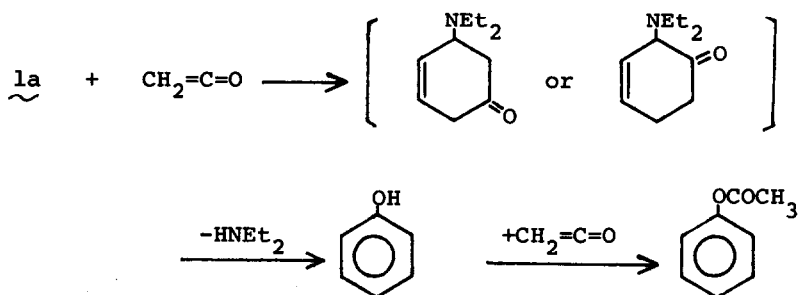
^eNeat. ^fIsolated yield. ^gYield determined by GLC.

suggests that the cycloaddition *exclusively* proceeds in such direction that two components with a partial charge-polarization attract each other.

Furthermore, we could obtain phenol derivatives by the reaction with ketene as the other reactive dienophile. For example, 1a was allowed to react with an excess amount of ketene in ether at 0°C to afford phenylacetate in 4% yield.



Scheme



We are presently investigating a general synthetic application by use of substituted 1,3-butadienes in addition to the one-step preparation of aromatic carboxylic acid esters and phenol derivatives.

References

- 1) S. Tanimoto, R. Schäfer, J. Ippen and E. Vogel, Angew. Chem., **88**, 643 (1976).
- 2) S. Tanimoto, Tetrahedron Lett., in press.
- 3) This substance was prepared according to the similar procedure to 1a using 3-methylcrotonaldehyde as a starting material: bp 63-65°/8.5 mmHg; NMR(CDCl₃) δ 6.00 (1H, d, 14 Hz), 4.92 (1H, d, 14 Hz), 4.40 (2H, m), 3.02 (4H, q, 7 Hz), 1.70 (3H, s) and 1.05 (6H, t, 7 Hz).